Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 16 (2012) 2060 – 2066

Energy Procedia

2012 International Conference on Future Energy, Environment, and Materials

Oxidation Rate of Sodium Sulfite in Presence of Inhibitors

Cui Shuai,Wang Lidong,Hao Siqi,Du Leixia

School of Environmental Science and Engineering, North China Electric Power University, Baoding, China

Abstract

Sulfur dioxide released by small scale industrial boilers has become the focus of environmental problems in the future. Sodium alkali desulphurization is a promising method, in which sulfite oxidation is of great importance. In the present work, Effect of several inhibitors on the oxidation rate of sodium sulfite was compared in a gas-liquid reactor. The results indicate that PT, a novel and nontoxic additive, is effective. The oxidation kinetics of sodium sulfite inhibited by PT was investigated by experiments. The reaction order of all reactants and activation energy were achieved, which provide the theoretical proof and practical reference for the recycling of the byproduct in sodium desulphurization process.

Keywords: oxidation rate; sodium sulfite;desulphurization; inhibitors

1. Introduction

Air pollution caused by sulfur dioxide has attracted much attention in China and the flue gas desulphurization installations are installed in power plants sequentially, especially for the limestone scrubbing. As a result, the acid rain is controlled to some extent. However, there are still over 500,000 units of industrial coal-fired boiler that emit large amounts of sulfur dioxide each year, just second to power plants. Therefore, it is significant to control the sulfur dioxide pollution caused by industrial boiler for improving the atmospheric quality of China.

Because the requirement for automation level is very critical and the process is complicated, the limestone desulphurization is difficult to be applied on the industrial boilers with small scales. Relatively, sodium alkali desulphurization has much advantage, in terms of high efficiency for sulfur dioxide removal, simple, low investment and energy consumption, and little scaling etc., which is being more and more applied in control of flue gas pollution from industrial boiler.

In the sodium alkali desulphurization, sodium hydroxide or sodium carbonate is used as absorbent. It reacts with SO_2 and produces sodium sulfite, which is an important resource in paper industry. However, sulfite is inevitably oxidized into sulfate in the process of desulphurization, transportation and storage

 doi:10.1016/j.egypro.2012.01.313

owing to the presence of oxygen in the flue gas or the air. Thus, it is necessary to develop effective inhibitor in order to prevent such oxidation process.

The previous work focused on the catalytic effect of transition metals[1], such as Co^{2+}, Mn^{2+}, and Cu^{2+}, on the reaction rate of sulfite oxidation[2-8]. However, the inhibited kinetic is yet to be investigated. In this paper, effects of several inhibitors were compared and PT was selected as an effective additive. The inhibited oxidation kinetics of sodium sulfite was studied by using a self-designed reactor. The reaction order of the reagents, activation energy and rate equation were achieved, which provide the theoretical proof and practical reference for the recycling of the byproduct in sodium desulphurization process.

2. Experimental

A bubbling apparatus is shown in Fig.1, which's used to observe the oxidation kinetics of sodium sulfite under the practical conditions. When 200 ml de-ionized water was added, inhibitor solution with know concentration was supplied into the reactor. The pure nitrogen, oxygen and air were blended in a known ratio by flow adjustment and injected into the reactor as oxidizing gas. Then the reaction was started, and a known amount of sodium sulfite was added to the reactor at the same time. Hydrochloric acid and sodium hydroxide were used to adjust pH. Some trace amount of reaction solution was taken out by pipette at intervals, being dissolved by hydrochloric acid and diluted to a desired volume then. The concentration of sulfate at different point of time was determined by barium sulfate spectrophotometry. Under the given conditions, the results indicated that the sulfate concentration increases linearly with the rise of reaction time. Thus the slop is the oxidation rate of sodium sulfite that reflects the relationship between sulfate concentration and reaction time.

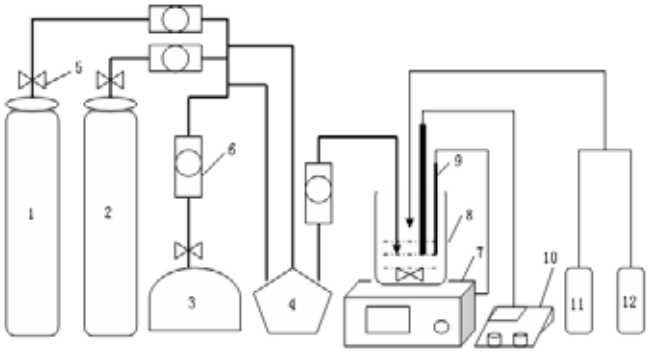

Fig.1. Apparatus of inhibited oxidation of sodium sulfite

1-pure nitrogen, 2-pure oxygen, 3-TYW-1 air compressor, 4-buffering bottle, 5-decompression valve, 6-LZB-4 glass rotameter, 7-85-2A magnetism heating mixer, 8-glass reactor in volume of 500 ml, 9-thermocouple, 10-PHS-3C pH meter, 11-hydrochloric acid solution in concentration of 3mol.L^{-1}, 12-sodium hydroxide solution in concentration of 1 mol.L^{-1}.

3. Results and discussions

3.1 Selection of inhibitors

As mentioned above, effects of three inhibitors, including formaldehyde, hyposulphite, and PT etc.,

were compared with the uninhibited one under the given conditions: initial concentration of sodium sulfite 10 g.L^{-1}, oxygen partial pressure 0.21 atm, gas flow rate 60 L.h^{-1}, rotation speed 860 rpm, pH 6.0, 45℃. The initial concentration of inhibitors was 0.214 mmol.L^{-1}.

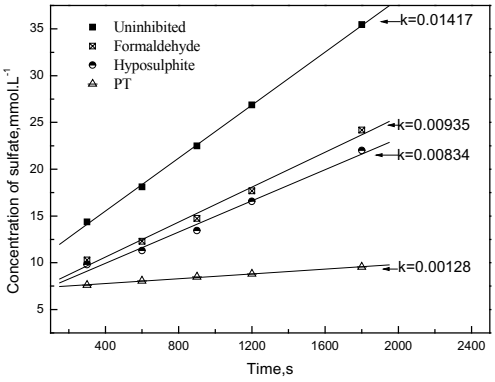

Fig.2. Screening of inhibitors by the comparison of reaction rate

Fig.2 showed that formaldehyde and hyposulphite have a little inhibition effect on the oxidation rate of sodium sulfite. However PT, having ring structures and linked with enolic hydroxyls, could slow down the reaction rate greatly. It might be due to the effect of hydroxyls that the ring becomes active and reductive, which results in absorption of the free radicals. Consequently, the chain reaction of sulfite oxidation was broken and inhibited.

3.2 Effect of PT concentration on the reaction rate

The initial concentration of PT was 0.107 mmol.L^{-1}, 0.214 mmol.L^{-1}, 0.429 mmol.L^{-1}, 0.858 mmol.L^{-1}, and 1.715 mmol.L^{-1}, respectively. Its effect on the oxidation rate was shown in Fig.3 and the other conditions were as following: initial concentration of sodium sulfite, oxygen partial pressure, gas flow rate and rotation speed were 10 g.L^{-1}, 0.21 atm, 60 L.h^{-1}, 860 rpm, pH 6.0, and 45℃, respectively.

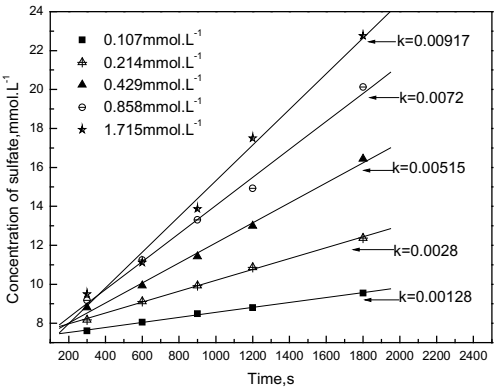

Fig.3. Effect of PT concentration on the reaction rate of sodium sulfite

Fig.3 indicated that the oxidation rate would decrease greatly with the rise of PT concentration. The concentration and reaction rate were of dimensionless with respect to the initial values. Thus the reaction order of PT, shown in Fig.4, was -0.70.

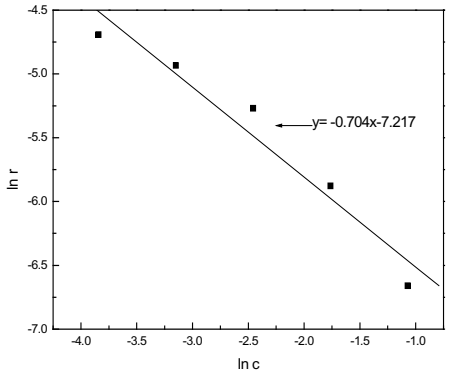

Fig.4. Reaction order of PT

3.3 Effect of sodium sulfite concentration on the reaction rate

Under the same conditions and an initial PT concentration 0.214 mmol.L^{-1}, the initial concentration of sodium sulfite was set as 5 g.L^{-1}, 10 g.L^{-1}, 20 g.L^{-1}, 40 g.L^{-1}, and 80 g.L^{-1}, respectively. Their effects on the reaction rate were determined (Fig.5).

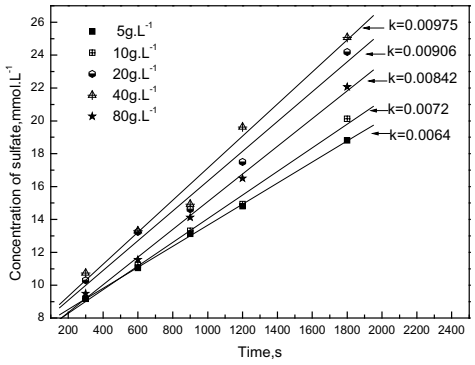

Fig.5. Effect of sodium sulfite concentration on the reaction rate

Fig.5 indicated that the oxidation rate would increase with the rise of sulfite concentration at 5 g.L^{-1} ~ 40 g.L^{-1}. The sulfite concentration and reaction rate were of dimensionless with respect to the initial values. Thus the reaction order of sodium sulfite, shown in Fig.6, was 0.20. However, it would decrease if the sulfite concentration continues to increase.

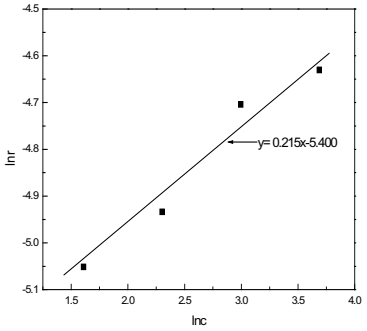

Fig.6. Reaction order of Sodium sulfite

3.4 Effect of oxygen partial pressure on the reaction rate

Under the same other conditions and the initial concentration PT 0.214 mmol.L^{-1}, the oxygen partial pressure was set as 0.05 atm, 0.10 atm, 0.21 atm, 0.50 atm, and 1.00 atm respectively. Effects of the oxygen partial pressure on the reaction rate were shown in Fig.7.

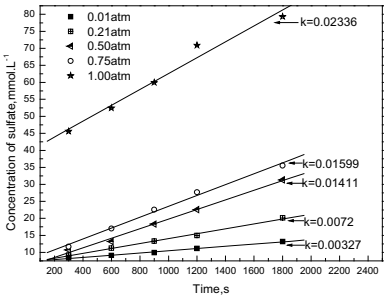

Fig.7. Effect of oxygen partial pressure on the reaction rate

According to Henry's law, the oxygen partial pressure is of proportion to the equilibrium concentration of oxygen at the gas-liquid phase interface. Fig.7 showed the reaction rate increases significantly with the rise of oxygen partial pressure. The reaction rate and oxygen partial pressure were of dimensionless with respect to the initial values and the reaction order of oxygen was 0.81 in Fig.8.

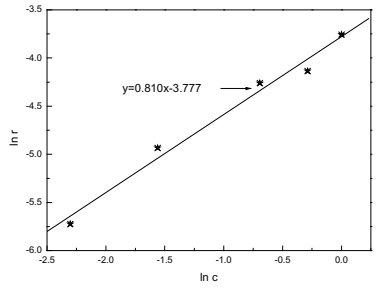

Fig.8. Reaction order of oxygen

3.5 Effect of temperature on the oxidation rate

Under the same other conditions, the temperature was set to 298K, 308K, 318K, and 328K respectively. Its effect on the reaction rate was shown in Fig.9. It indicated that the reaction rate would increase greatly with the rise of temperature.

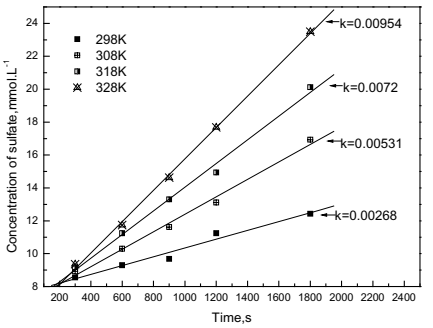

Fig.9. Effect of temperature on the reaction rate

Plot of logarithm of the reaction rate against 1/T was shown in Fig 10, indicating that the effect of temperature on the reaction rate complies with Arrhenius law in the range from 298K to 318K. According to the slope of regression curve, the apparent activation energy is 33.6kJ.mol^{-1}.

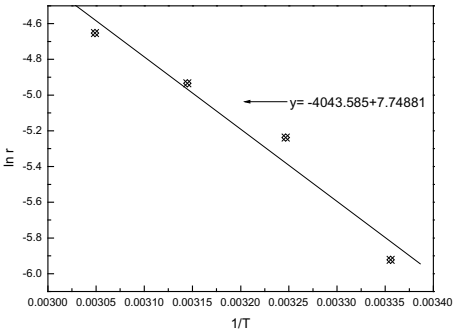

Fig.10. Apparent activation energy of the sodium sulfite oxidation inhibited by PT

In our previous research, the general reaction in absence of inhibitors was controlled by oxygen diffusion. Consequently, it was influenced by the intrinsic reaction rate and solubility of oxygen simultaneously, resulting in small apparent activation energy[9] of 6.46 kJ.mol^{-1}. However, owing to the inhibition effect of PT, the general reaction rate might become to depend on the intrinsic reaction that would be sensitive to the reaction temperature, resulting in higher apparent activation energy.

4. Conclusions

1）Effect of three inhibitors on the oxidation rate of sodium sulfite were compared in a self-designed bubbling apparatus. The results showed that PT is the most effective.

2）The inhibited oxidation kinetics in presence of PT were investigated. The reaction order for sodium sulfite, oxygen partial pressure and PT are 0.20, 0.80 and -0.70 respectively.

3）The activation energy was obtained to be 33.6kJ.mol^{-1} by changing the temperature. It might be due to the effect of hydroxyls that the ring becomes active and reductive, which results in absorption of the free radicals. Consequently, the chain reaction of sulfite oxidation was broken and inhibited.

Acknowledgment

The present work is supported by the National High Technology Research and Development Program of China (No. 2007AA061703) and the Key Project of Chinese Ministry of Education (No. 109157) and the Fundamental Research Funds for the Central Universities (No. 10MG35).

References

[1] A. Lancia, D. Musmarra, F. Pepe, M. Prisciandaro, "Model of oxygen absorption into calcium sulfite solutions, "Chemical Engineering Journal, vol. 66, 1997, pp. 123-129

[2] C. H. Barron, H. A. O'Hern, "Reaction kinetics of sodium sulfite oxidation by the rapid-mixing method," Chemical Engineering Science, vol. 21,1966, pp. 397-404.

[3] A.N.Ermakov, A.P.Purmal, "Catalysis of HSO_3^-/SO_3^{2-} oxidation by manganese ions, " Kinetics and Catalysis, vol. 43, 2002, pp. 249-260.

[4] G. Kracker-Semler, R. Marr, M. Siebenhofer, "Experimental investigation and modeling of catalytically supported sulfite/bisulfite oxidation with oxygen," Chemical Engineering Technology, vol .27, 2004, pp. 630-633.

[5] D. Karatza, M. Prisciandaro, A. Lancia, D. Musmarra, "Reaction rate of sulfite oxidation catalyzed by cuprous ions," Chemical Engineering Journal ,vol. 145, 2008, pp.285-289.

[6] Z. Bo, "Study on the reaction rate of sulfite oxidation with cobalt ion catalyst," Chemical Engineering Science,vol. 60, 2005, pp. 863-868.

[7] A. A. Shaikh, S. M. J. Zaidi, "Kinetics of catalytic oxidation of aqueous sodium sulfite," Reaction Kinetics and Catalysis Letters, vol. 64, 1998, pp. 343-349.

[8] V.Linek, V.Vacek, "Chemical engineering use of catalyzed sulfite oxidation kinetics for the determination of mass transfer characteristics of gas-liquid contactors," Chemical Engineering Science, vol. 36, 1981, pp.1747-1768.

[9] W. Lidong, M. Yongliang, Y. Gang, Z. Wendi, Z. Yabin, H. Jiming, "Mechanism and kinetics of uncatalyzed oxidation of magnesium sulfite under heterogeneous conditions," Scientia Sinica Chimica, vol. 40, 2010, pp. 1172-1178.